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RESEARCH OF THE ELECTRICAL PROPERTIES OF THE INTERCRYSTALLITE BOUNDARY AND MECHANISMS OF CONDUCTIVITY IN A ZnO VARISTOR WITH IMPURITIES

BY

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Abstract:
The article describes the electrical properties of the intercrystallite boundary and mechanisms of conductivity in a ZnO varistor with impurities. The study shows the properties of the reagents used in the synthesis of the ZnO varistor, as well as the composition of the substances used to provide the varistor effect. The article also presents the energy diagrams of the crystallite boundary in the ZnO varistor, the equivalent circuit diagram, and the energy diagram of microvaristors, respectively. It has been established that conductivity is possible during physical processes both at the intercrystallite boundary and through a potential barrier. And also, the dependence of conductivity on frequency and temperature was shown. It turned out that in the low-frequency region, the electrical conductivity increases monotonically, and then strongly increases with increasing frequency. In this case, the electrical conductivity σ *changes according to the law* $\sigma \approx f^{0.8}$*. The resulting dependence* $\sigma \approx f^{0.8}$ *indicates a hopping mechanism of charge transfer over states localized in the vicinity of the Fermi level [1]. Dependence of conductivity on temperature, it can be said that the charge transfer in the varistors under study is carried out by hopping conduction of electrons with a variable hopping length over localized states lying in a narrow energy band near the Fermi level. These states in a varistor can be created by extended defects—intercrystallite boundaries and dislocations.*

Keywords: *ZnO varistors, impurities, potential barrier, crystallite, microvaristors, energy circuit, non-linearity, electrical conductivity, frequency, temperature.*

INTRODUCTION

It is known that semiconductor materials are of great importance for power engineering due to their non-linear conductivity. The use of such materials provides attenuation of harmful voltage waves, which can be amplified during power surges on high-voltage lines and half-stations. It should be noted that SiC and ZnO materials with symmetrical current-voltage characteristics are mainly used for this purpose in modern electrical engineering. characteristics. The material based on these elements (at operating voltages) as a dielectric has a high resistance. With a sharply decreasing resistance, it has a conductive property, i.e. varistor property. If we connect such an element, for example, a transformer, in parallel to our protective device, then the sharply rising waves will decrease, and the device will not detect high transient voltages[2].

One of the factors that distinguishes ZnO ceramics from a varistor is the wide variation in its basic electrophysical parameters due to the introduction of a small amount of impurities into them.

It should be noted that one of the most promising areas for the development of protective devices and elements is the creation of two-phase and multiphase composite materials based on a ceramic varistor[7-16].

METHOD OF ANALYSIS

For the manufacture of varistors, a ceramic charge of the composition (mol.%) 96,5 ZnO+ 0,5+Bi_2O3+ 0,5 Co_3O_4 + 0,5 MnO_2 +0,5 B_2O3 + 1 Sb_2O_3 + 0,5 ZrO_2 in an amount of 100 g is weighed and crushed in a ball mill to a particle size of 60 microns or less. Then, granules are prepared from this mixture, which are pressed under a force of 40-ton force to obtain samples in the form of washers 10 mm high and 20 mm in diameter. After that, the samples are placed in an electric furnace for synthesis: heating to a temperature of 900°C is carried out at a rate of 150°C/h and to a temperature of 1250°C - at a rate of 200°C/h.

The properties of the reagents used and the composition of the varistor samples are shown in tables 1 and 2.

Table1.
Properties of reagents used

Properties	**ZnO**	**Bi_2O_3**	**Co_3O_4**	**Sb_2O_3**	**MnO_2**	**Ni_2O_3**	**CrO_3**	**H_3BO_3**
Quan.of maincomponent,mas. %	99,96	99,97	99,97	99,96	99,95	99,93	99,93	99,96
Degree of dispersion, µm	0,3	5-10	0,5-2	0,2-1	0,3-3	0,5-4	0,5-2	0,5-3
Density10^3 kg/m^3	5,6	8,9	5,68	5,2	5,18	7,45	4,98	3,2
Melting points,ºC	1975	817	1805	655	1785	1957	break.	break.
Cation radius,mm	0,074	0,098	0,072	0,090	0,080	0,069	0,052	-
Type of electrical conductivity	n	p	p	p	p	p	p(Cr_2O_3)	p

Table2.
Composition of varistor samples

Ingredient	**Sample №1**		**Sample №2**		**Sample №3**	
	mol%	Quantity in 500 grams	mol%	Quantity in 500 grams	mol%	Quantity in 500 grams
ZnO	97	91,6	96,5	90,76	95,5	89,577
Bi_2O_3	0,5	2,7	0,5	2,69	0,5	2,6845
Sb_2O_3	1	3,4	1	3,368	1	3,359
Co_3O_4	0,5	1,398	0,5	1,392	0,5	1,3887
B_2O_3	0,5	0,41	0,5	0,404	0,5	0,403
MnO_2	0,5	0,51	0,5	0,502	0,5	0,4955
Cr_2O_3	-		0,5	0,878	0,5	0,876
Ni_3O_2	-	-	-	-	0,5	0,522
SiO_2	-	-	-	-		0,692

Synthesis of pressed washers takes place in atmospheric air, and the washers are annealed at a temperature of 1200°C for 2 hours. After turning off the oven, the samples are cooled for 7–8 hours. These surfaces are vacuum-deposited with a thin layer (3–4 mm) of aluminum to provide electrical contact.

The height of the intergranular barrier φ_0=0,8 eV in ZnO oxides with surface-active ions (Bi, Co, Mn). The addition of ZnO to these ions complicates its structure. For example, when trivalent Ca is added to ZnO, adsorption surfactant centers are formed. The resulting this structure can localize free electrons [Ca^{3+}-O_2^-] Numerous experimental results show that the potential crystal barrier in ZnO stabilizes only in the range of 350-400^0 C, regardless of the type of impurity. In general, it is necessary to determine the mechanism of physical processes in bipolar conduction devices, to ensure the use of varistor materials for various purposes, and the stability of their properties[8].

When choosing various functional varistes made of semiconductor ceramic materials (for example, ZnO, SiC), it is necessary to take into account their crystalline conductivity, band gap, electrical conductivity of electric charges, and potential amplitudes at the interface between amorphous and crystalline phases. Consider the process of moving charge carriers in ZnO, which differs from a number of other semiconductor materials.

The process of moving electric charges in polycrystalline semiconductor ceramics based on ZnO is divided into two groups:
- the movement of electrons through a potential barrier;
-along the border of a potential barrier.

The first mechanism is the conversion of electrical carriers from crystallites to crystalline ones, and the second mechanism is breakthrough displacements. Despite the differences in voltage ranges and types of materials, the only working element of all ceramic varistors with a fuzzy structure is the crystallite boundary. Figure 1 shows the inter-crystalline potential barrier

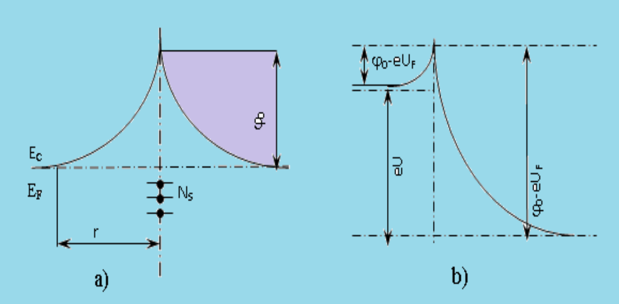


Figure 1. Eenergy circuit of the crystallite boundary a) U=0; b) U>0

A potential barrier was formed as a result of the exchange of electrons with two neighboring crystallites and an amorphous phase (intercrystallite boundary) between them (Fig. 1b). In equilibrium, the charges on the crystallite surface are compensated by electrons stabilized in the amorphous phase, i.e.

$$eN_S = 2eN_d r \quad (1)$$

and the height of the potential barrier is determined by the ratio [2-6]:

$$\varphi_0 = eN_d r^2 / 2\varepsilon_0 \varepsilon_r = e^2 N_S{}^2 / 2\varepsilon_0 \varepsilon_r N_d \qquad (2)$$

Here:

r - the width of the surface charge formation region;

d - average crystallite size;

N_S -crystallite density;

N_d - donor concentration;

ε_0 -electric constant ($\varepsilon = 8{,}85 \cdot 10^{-2} F/m$);

ε_r -relative permeability;

e - electron charge ($1{,}6 \cdot 10^{-19}$ Kl);

With r“d” and eN_S “$eN_d \cdot d/2$” crystallites decreased relatively.

The electrical conductivity of crystallites with high conductivity, overcoming the potential barrier, is determined by the formula

$$\sigma_\varphi = \frac{1}{N_\sigma} \sigma_V \exp(-\varphi_0 / kT) \qquad (3)$$

Here N_σ - the number of charge carriers that have overcome the electric barrier with height φ_0.

$\sigma_V = e\, n\, \mu_V$ - special conductivity of crystallites;

μ_V - charge electric charge carriers;

n - concentration of portable electric charges.

The exponential sign is the temperature dependence of the speed of an electric charge carrier on temperature.

Figure 2 shows the energy diagram of the intergranular boundary (a) and the equivalent electric circuit (b), as well as energy diagrams in microvaristors (a, b, c).

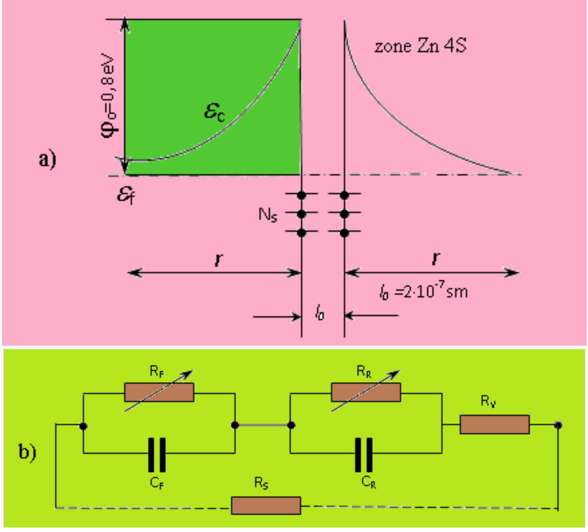


Figure 2. Energy diagram of the crystallite boundary (a) and equivalent electrical circuit (b)

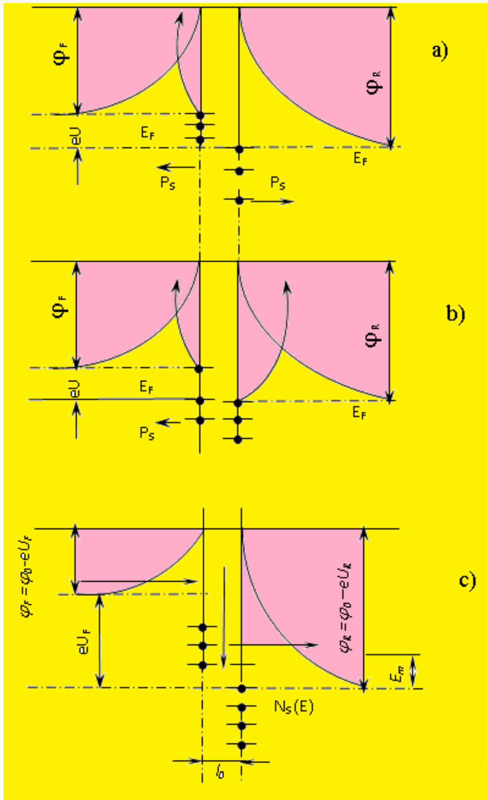


Figure3. Energy circuit microvaristor

a) $E < E_i$; b) $E > E_i$;c) - $E > E_a$

At present, ZnO-based varistors are widely used in high-voltage technology to limit the increase in voltage (current) caused by various reasons. The non-linearity (β) of the current-voltage voltage (U_{op}) of ZnO-based cells varies in the range of 50-70. This high non-linearity makes ZnO varistors indispensable compared to other semiconductors[4]. ZnO varistors are connected in series and placed in a dielectric coating. One of the most important factors in the application of varistors is the stability of their parameters. To do this, electrothermal wear of the varist is carried out: under the influence of an electric field, the barriers are heated to 403–423 K, and then cooled to room temperature. To protect them from the environment, the surface of the electrodes is varnished. This process is repeated until the varistor opening voltage (U_{op}), non-linearity factor (β), and resistance (ρ) to the opening voltage stabilize. It is important that the varistor settings are protected from moisture in order for them to remain stable. The last operation of varistors is to place electrodes on their surface. The process is carried out as follows: the surface of the elements is chemically cleaned, silver pastes are placed on the surface and fired. To protect the electrodes from the environment, their surface is polished. ZnO is a semiconductor compound and is type A^2 B^6 [3].

The corresponding parameters of SiC, its band gap is larger than that of other semiconductors. Therefore, the non-linearity of the original ZnO must be greater after its opening voltage, since its coefficient of non-linearity is smaller. However, despite the band gap, due to the lack of oxygen during the firing process, the stoichiometry of ZnO is distorted and therefore has an n-type semiconductor. A very thin insulating region is formed among the ZnO crystallites, which ensures the formation of the varistor effect. The ZnO varistor, with a cross-section of 1 cm^2, has a constant amplitude of several kA and can withstand high voltage surges up to the operating voltage.

When studying the transport characteristics of inhomogeneous materials, an important role is given to the analysis of the dispersion of the dielectric parameters of the material (dielectric permittivity, dielectric losses, etc.). The dependences of the effective values of the permittivity and the dielectric loss factor on frequency are sensitive to the relationship between the electrical parameters of the dispersed phase and the matrix, as well as to the shape of the inclusions and their orientation in an external electric field.

Despite the wide range of applications in various fields of physics and chemistry [6;10;15], theoretical studies of the dispersion of the permittivity of heterogeneous media are hindered for a number of reasons, among which the following should be noted. Analytical calculations of the effective parameters of multi-component systems, which are of independent importance and are an integral part of the theory of dispersion of inhomogeneous dielectrics, are in themselves a complex mathematical problem that can be solved only in individual cases.

Note that the frequency dependence of the dielectric parameters, namely, the components of the complex permittivity, is a characteristic of the material and is determined for each substance not only by the properties of the material's molecules but by the presence and composition of impurities.

Figure 4 shows the conductance as a function of frequency.

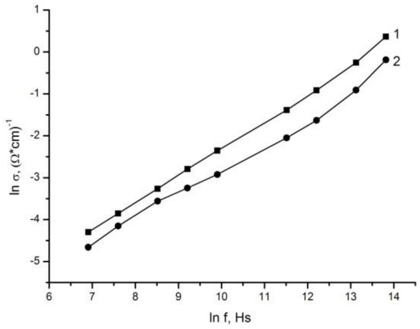
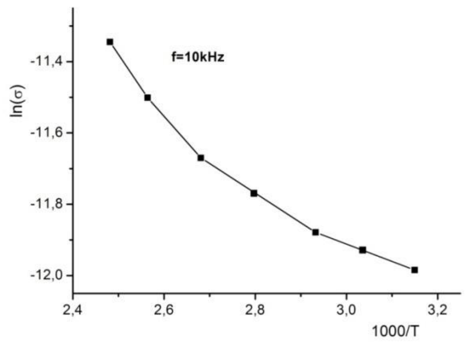


Figure 4. Dependence conductivity from frequency
1-303K, 2-344K

Figure 4 shows that in the low-frequency region, the electrical conductivity increases monotonically, and then increases strongly with increasing frequency. In this case, the electrical conductivity σ changes according to the law $\sigma \approx f^{0.8}$. The dependence $\sigma \approx f^{0.8}$obtained indicates a hopping mechanism of charge transfer over states localized in the vicinity of the Fermi level [1]. Note that at the temperatures under study, the σ=F(f) dependence has the same character.

Figure 5 shows the temperature dependence of conductivity at f=10kHz.



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